

# Electrostatic interaction energies of homogeneous cubic charge distributions

Hanno Essén  
Department of Mechanics  
Royal Institute of Technology  
S-100 44 Stockholm, Sweden

February 2, 2008

## Abstract

The starting point is the problem of finding the interaction energy of two coinciding homogeneous cubic charge distributions. The brute force method of subdividing the cube into  $N^3$  sub-cubes and doing the sums results in slow convergence because of the Coulomb singularity. Using symmetry and algebra the Coulomb singularities can be eliminated. This leads to an accurate numerical algorithm as well as an interesting exact result relating the desired interaction energy to three other interaction energies, namely those of cubes touching each other at a face, at an edge, and at a corner, respectively. As an application a simple model illustrating Wigner crystallization is presented.

# 1 Introduction

There are still many interesting problems involving the electrostatics of cubic geometries. These have to do with cubic ionic crystals [1, 2], with the force and potential from cubic charge and mass distributions [3, 4, 5, 6], and with the electric capacitance of the cube [7, 8]. Here we will discuss the evaluation of the electrostatic interaction energy of two coinciding homogeneous cubic charge distributions. For unit charge distributions in unit cubes this energy is given by,

$$C = \int_{V_1} \int_{V_2} \frac{dV_1 dV_2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (1)$$

where,  $\mathbf{r}_a = (x_a, y_a, z_a)$ , and

$$V_a = \{(x_a, y_a, z_a); 0 < x_a < 1, 0 < y_a < 1, 0 < z_a < 1\}, \quad a = 1, 2. \quad (2)$$

This integral arises naturally in the free electron gas theory of conduction electrons in metals, see Raimis [9]. Its actual value is usually not needed for most applications of that theory. In an extension of the theory by Essén [10], however, it is needed. Another application of this type of integral will be given below. The value of  $C$  can be calculated exactly. Put,

$$\phi_C(\mathbf{r}) = \int_{V_2} \frac{dV_2}{|\mathbf{r} - \mathbf{r}_2|}, \quad (3)$$

for the electrostatic potential energy from a homogeneous cubic charge distribution. This potential has been discussed by Waldvogel [3], by Hummer [5], and by Seidov and Skvirsky [6]. Using it we can write (1) in the form,

$$C = \int_{V_1} \phi_C(\mathbf{r}_1) dV_1, \quad (4)$$

and this makes it possible to find the analytical expression,

$$C = -2 \left\{ \frac{2\sqrt{3} - \sqrt{2} - 1}{5} + \frac{\pi}{3} + \ln [(\sqrt{2} - 1)(2 - \sqrt{3})] \right\}, \quad (5)$$

(Seidov and Skvirsky [6]). This evaluates to,

$$C \approx 1.8823126443896601600 \quad (6)$$

using twenty digits. Another expression for  $C$  in terms of a one dimensional integral has been derived by Essén and Nordmark [1].

If we displace one of the cubes in (2) one unit along the  $x$ -axis the integral (1) changes into an integral for the interaction energy of cubes with one face

touching (see Fig. 1). Let us call this integral  $C_f$ . If we displace one cube one unit along both the  $x$  and the  $y$ -axis we get the integral for cubes with an edge in common, call it  $C_e$ . If we finally displace one of the cubes one unit along all three directions of space we get the integral for cubes touching at one corner, call it  $C_c$ . One of the results found below then says that,

$$C = C_f + C_e + \frac{1}{3}C_c. \quad (7)$$

This might be a new result.

Coulomb interaction energy integrals find one of their main applications in Hartree and Hartree-Fock self-consistent field studies of many electron systems, see for example Raimes [9]. As an application of the results of this paper we use them for crude estimates of the energy of electrons moving in a cubic background of smeared out positive charge. In particular we compare the energies of delocalized electron states with those of localized states. When the density is small the localized states are found to have lower energy. This is the phenomenon of Wigner crystallization [11, 12].

## 2 The brute force approach

Consider two electrons of charge  $e$  in a cubic box with edges of length  $L$ . Assume that both electrons have constant charge density,

$$\rho = e/L^3, \quad (8)$$

in this box. The Coulomb, electrostatic, interaction energy of these charge distributions is then:

$$C \frac{e^2}{L} = \left(\frac{e}{L^3}\right)^2 \int_{\mathbf{r}_1 \in V_1} \left( \int_{\mathbf{r}_2 \in V_2} \frac{dV_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) dV_1. \quad (9)$$

Here  $V_a$ , ( $a = 1, 2$ ) denote the cubic boxes over which the integration variables,  $\mathbf{r}_a = (x_a, y_a, z_a)$ , take their values. We now introduce units so that  $e = L = 1$ . The integral can then be expressed in the form,

$$C = \int_{x=0}^{x=1} \int_{y=0}^{y=1} \int_{z=0}^{z=1} \int_{u=0}^{u=1} \int_{v=0}^{v=1} \int_{w=0}^{w=1} \frac{dx dy dz du dv dw}{\sqrt{(x-u)^2 + (y-v)^2 + (z-w)^2}}, \quad (10)$$

which shows explicitly that this is a six-dimensional integral.

Nowadays we are spoilt by systems for doing mathematics by computer. It is therefore tempting to try these systems whenever some cumbersome

integral arises, and frequently they do deliver sensible answers. For the integral (10), however, those that I have tried fail. Brute force can't handle the Coulomb singularity. Let us see what happens if we start by dividing each cube into  $N^3$  sub-cubes:

$$V_{aN}^{ijk} = \left\{ (x_a, y_a, z_a); \frac{i-1}{N} < x_a < \frac{i}{N}, \frac{j-1}{N} < y_a < \frac{j}{N}, \frac{k-1}{N} < z_a < \frac{k}{N} \right\}, \quad (11)$$

where the indices,  $i, j$ , and  $k$ , run from 1 to  $N$ . Our integral can then be written as the sum,

$$C = \sum_{ijk=1}^N \sum_{lmn=1}^N C_{N,ijk}^{lmn}, \quad (12)$$

over  $N^6$  terms, integrals over pairs of sub-cubes,

$$C_{N,ijk}^{lmn} = \int_{V_{1N}^{ijk}} \int_{V_{2N}^{lmn}} \frac{dV_1 dV_2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (13)$$

For sufficiently large  $N$  most integrals are over pairs of spatially separated sub-cubes and can be easily approximated. This leads to a brute force approach. Fairly large contributions should, however, come from pairs of cubes that coincide or touch since they are strongly affected by the singularity. Such an approach is clearly clumsy.

### 3 Removing the interior singularity

The awkward singularity occurs only in the interior of those  $N^3$  terms of this sum for which the integration sub-cubes are equal. If we thus write,

$$C = \sum_{ijk=1}^N C_{N,ijk}^{ijk} + \sum_{ijk=1}^N \sum_{lmn=1}^N{}' C_{N,ijk}^{lmn}, \quad (14)$$

where the terms with all three indices the same ( $i = l, j = m, k = n$ ) are excluded in the double sum, we see that the interior singularities occur in the first sum over coinciding sub-cubes. But these integrals are all identical and equal to,

$$C_N = C_{N,111}^{111} = \int_{V_{1N}^{111}} \int_{V_{2N}^{111}} \frac{dV_1 dV_2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (15)$$

From formula (14) one thus gets,

$$C = N^3 C_N + \sum_{ijk=1}^N \sum_{lmn=1}^N{}' C_{N,ijk}^{lmn}. \quad (16)$$

Apart from being over a smaller cube, the integral  $C_N$  is essentially like the original integral. In fact one easily finds the scaling property,

$$C = N^5 C_N. \quad (17)$$

Using this equation (16) becomes,

$$C = \frac{C}{N^2} + \sum_{ijk=1}^N \sum_{lmn=1}^N{}' C_{N,ijk}^{lmn}. \quad (18)$$

Solving for  $C$  we thus finally have,

$$C = \frac{N^2}{N^2 - 1} \sum_{ijk=1}^N \sum_{lmn=1}^N{}' C_{N,ijk}^{lmn}. \quad (19)$$

Here the original integral with its singularity has been written as a sum of  $N^6 - N^3$  integrals without (interior) singularities.

## 4 Approximating the non-diagonal integrals

The non-singular integrals can be approximated by the product of the two cubic volumes divided by the distance between their midpoints. A simple calculation gives,

$$C_{N,ijk}^{lmn} = \int_{V_{1N}^{ijk}} \int_{V_{2N}^{lmn}} \frac{dV_1 dV_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \approx \frac{1}{N^5} \frac{1}{\sqrt{(i-l)^2 + (j-m)^2 + (k-n)^2}}. \quad (20)$$

If we introduce the notation, compare equation (17),

$$C_{ijk}^{lmn} \equiv N^5 C_{N,ijk}^{lmn}, \quad (21)$$

we now have,

$$C = \frac{1}{N^3(N^2 - 1)} \sum_{ijk=1}^N \sum_{lmn=1}^N{}' C_{ijk}^{lmn}. \quad (22)$$

Since the number of terms in the sum grows as  $N^6$  it is of interest to take advantage of symmetries to reduce it as much as possible. Doing this we find that,

$$C = \frac{12}{N^3(N^2 - 1)} \left( \frac{N^2}{2} \sum_{l < i}^N C_{i11}^{l11} + N \sum_{m < j}^N \sum_{n < k}^N C_{1jk}^{1mn} + \frac{2}{3} \sum_{l < i}^N \sum_{m < j}^N \sum_{n < k}^N C_{ijk}^{lmn} \right). \quad (23)$$

$N$	$C_N^0$	$C_N^0 - C$
2	1.899556871	$2 \cdot 10^{-2}$
4	1.887296187	$5 \cdot 10^{-3}$
8	1.883654361	$1 \cdot 10^{-3}$
16	1.882660569	$3 \cdot 10^{-4}$
$\vdots$	$\vdots$	$\vdots$
$\infty$	1.882312644	0

Table 1: This table illustrates the slow convergence of  $C_N^0$ . Note that computation time goes as  $N^6$ .

is an alternative way of writing equation (22). Putting,

$$\Delta_{ijk}^{lmn} \equiv \sqrt{(i-l)^2 + (j-m)^2 + (k-n)^2}, \quad (24)$$

we have that,

$$C_{ijk}^{lmn} \approx 1/\Delta_{ijk}^{lmn}, \quad (25)$$

assuming that  $(i, j, k) \neq (l, m, n)$ . If we put this into (22), or (23), we get,

$$C \approx C_N^0 \equiv \frac{1}{N^3(N^2-1)} \sum_{ijk=1}^N \sum_{lmn=1}^N \frac{1}{\Delta_{ijk}^{lmn}} = \quad (26)$$

$$\frac{12}{N^3(N^2-1)} \left( \frac{N^2}{2} \sum_{l<i}^N \frac{1}{\Delta_{i11}^{l11}} + N \sum_{m<j}^N \sum_{n<k}^N \frac{1}{\Delta_{1jk}^{1mn}} + \frac{2}{3} \sum_{l<i}^N \sum_{m<j}^N \sum_{n<k}^N \frac{1}{\Delta_{ijk}^{lmn}} \right). \quad (27)$$

The smaller the box, the smaller the error, so there is hope that this expression will converge to the correct value of  $C$  when  $N$  goes to infinity, i.e. that

$$C = \lim_{N \rightarrow \infty} C_N^0. \quad (28)$$

The approximation (25) then immediately gives the following estimate for  $C$ , when  $N = 2$ ,

$$C \approx C_2^0 = 1 + \frac{1}{\sqrt{2}} + \frac{1}{3} \frac{1}{\sqrt{3}} \approx 1.899556871, \quad (29)$$

a value which turns out to be correct to two significant digits. This is encouraging but the convergence for increasing  $N$  is slow, see Table 1. When  $N = 16$  the error is still  $3 \cdot 10^{-4}$ . The exact value is from Eqs. (5) and (6).

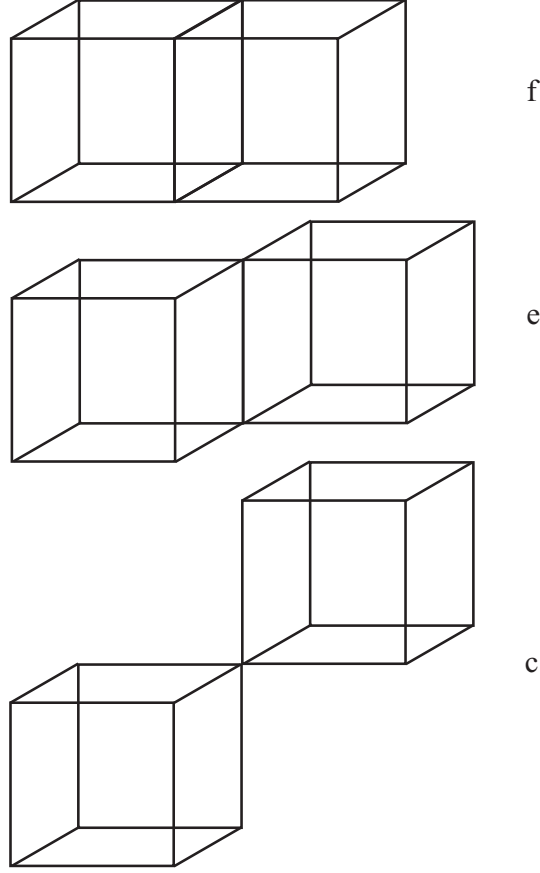


Figure 1: This figure illustrates the three cases of touching cubes for which the integrand is singular on a face, an edge, and a corner, respectively.

## 5 Removing the remaining singularity

We now introduce the symbols,

$$C_{l,1,1}^{l+1,1,1} \equiv C_f, \quad C_{1,m,n}^{1,m+1,n+1} \equiv C_e, \quad C_{l,m,n}^{l+1,m+1,n+1} \equiv C_c, \quad (30)$$

for the integrals between adjacent sub-cubes that have a face, an edge, and a corner, in common, respectively (see Fig. 1). These represent the terms in the sum (23) that still are affected by the Coulomb singularity. Using this notation formula (23) for the case  $N = 2$  gives,

$$C = C_f + C_e + \frac{1}{3}C_c, \quad (31)$$

which is the result (7) promised in the introduction.

The integrals (30) occur in the sum (23) for  $C$  the following number of times,

$$N_f = 6N^2(N-1), \quad N_e = 12N(N-1)^2, \quad N_c = 8(N-1)^3, \quad (32)$$

respectively. Let us put,

$$F_N \equiv \frac{N_f}{N^3(N^2-1)} = \frac{6}{N(N+1)}, \quad (33)$$

$$E_N \equiv \frac{N_e}{N^3(N^2-1)} = \frac{12(N-1)}{N^2(N+1)}, \quad (34)$$

$$C_N \equiv \frac{N_c}{N^3(N^2-1)} = \frac{8(N-1)^2}{N^3(N+1)}, \quad (35)$$

and define the two quantities,

$$\delta_N \equiv C_N^0 - F_N - E_N \frac{1}{\sqrt{2}} - C_N \frac{1}{\sqrt{3}}, \quad (36)$$

and, using this,

$$C_N^1 \equiv \delta_N + F_N C_f + E_N C_e + C_N C_c. \quad (37)$$

Clearly  $\delta_N$  is the sum of the terms in (26) that approximate integrals that do not contain singularities (in the interior or on the boundary). We thus have that  $\delta_2 = 0$  since for  $N = 2$  all the sub-cubes are in contact. Therefore  $C_N^1$  is an estimate of the integral  $C$  by a sum in which the integrals containing surface singularities have been replaced by their (unknown) exact values, while the remaining ones are estimated by their inverse distance, Eq. (25).

The function  $C_N^1$  obeys both (since  $\delta_2 = 0$ ),

$$C_2^1 = C, \quad (38)$$

and,

$$\lim_{N \rightarrow \infty} C_N^1 = C. \quad (39)$$

Since the  $\delta_N$  are known quantities the assumption that  $C_N^1 = C$ , in equation (37), gives for each  $N$  an equation in four unknowns ( $C, C_f, C_e, C_c$ ). A system of four such equations,

$$C - F_{N_k} C_f - E_{N_k} C_e - C_{N_k} C_c = \delta_{N_k} \quad k = 1, 2, 3, 4, \quad (40)$$

can thus be solved for these unknowns. Now, each quadruple of numbers  $N_1, N_2, N_3, N_4$ , will give us an estimate of the four integrals. In calculating the  $\delta_{N_k}$  the approximation (25) has only been used for integrals in which



$N_1$	$N_2$	$N_3$	$N_4$	$C^1$	$C_f^1$	$C_e^1$	$C_c^1$
2	3	4	5	1.882304130	0.98272866	0.70632105	0.57976327
2	6	8	10	1.882311519	0.98306698	0.70575406	0.58047142
2	11	15	19	1.882312489	0.98340873	0.70521257	0.58107356
2	20	25	30	1.882312615	0.98367876	0.70479560	0.58151474
2	30	35	40	1.882312641	0.98390505	0.70445014	0.58187235
2	44	50	56	1.882312647	0.98409569	0.70416088	0.58216823

Table 2: The rows of this table illustrate solutions of the system of equations (40).  $C^1$  has converged to  $C$  in the last rows but the convergence to the other three integrals is clearly slow.

the integrand does not become singular. Obviously one of the numbers  $N_k$  should always be chosen to be two since then one of the equations of the system is exact.

In Table 2 some results of this approach are shown. After finding four different sets of quantities a standard linear equation solver delivers four solutions to the linear set of equations. For  $C$  this is clearly seen to give excellent values. The three other integrals converge much more slowly but seem to approach  $C_f \approx 0.984$ ,  $C_e \approx 0.704$ , and  $C_c \approx 0.582$ , respectively.

## 6 Electrons in a homogeneous cube

Here we will use crude estimates of the Hartree energy [9] of electrons that move in a cube of homogeneous positive charge density. Using this crude theory we will investigate whether the electrons tend to delocalize in the cube or if a state with localized electrons has lower energy.

We assume that the electrons either are delocalized in the cube and have constant charge density in the cube or that they localize in one octant of the cube and have constant charge density there. This means that we can treat either 8 electrons or 8 electron pairs. With these assumptions the electrostatic interaction energy can be found from the results above. The kinetic energy is estimated essentially by means of the uncertainty principle and the Pauli exclusion principle.

We start with 8 electrons in delocalized states. They are assumed to move in a cube of side  $L$  and positive charge  $8e$ . The energy is then the sum of the kinetic energy,

$$T_{8d} = \frac{\hbar^2}{2m} \left[ 2 \frac{3}{L^2} + 6 \left( \frac{2}{L^2} + \frac{1}{(L/2)^2} \right) \right], \quad (41)$$

and the electrostatic energy,

$$V_{8d} = \frac{1}{2} \frac{(8e)^2}{L} C - 8 \frac{8e^2}{L} C + \frac{8 \cdot 7}{2} \frac{e^2}{L} C. \quad (42)$$

In the kinetic energy the two first electrons are assumed delocalized over the cube without nodes in the wave function. The remaining six must then go into the three degenerate states with one node. The first term in the electrostatic energy is the self energy of the positive background. Then follows the attraction between the background and the eight delocalized electrons. The final term is the sum of the  $8 \cdot 7/2$  electron-electron pair repulsion terms. Simplifying this gives the total energy

$$E_{8d} = \frac{\hbar^2}{2m} \frac{42}{L^2} - C e^2 \frac{4}{L}. \quad (43)$$

The energy of this closed shell delocalized state should now be compared to the energy of the ferromagnetic localized state with the electrons in one corner each. We find,

$$T_{8l} = \frac{\hbar^2}{2m} 8 \frac{3}{(L/2)^2} = \frac{\hbar^2}{2m} \frac{96}{L^2}, \quad (44)$$

for the kinetic energy since all 8 electrons now sit in cubes (octants) of side  $L/2$ . They are however alone in their corners (octants) so the Pauli principle is automatically obeyed. The electrostatic energy becomes

$$V_{8l} = \frac{1}{2} \frac{(8e)^2}{L} C - 8 \frac{e^2}{L/2} (C + 3C_f + 3C_e + C_c) + \frac{8}{2} \frac{e^2}{L} (3C_f + 3C_e + C_c). \quad (45)$$

Simplification of this using Eq. (31) gives the total energy

$$E_{8l} = \frac{\hbar^2}{2m} \frac{96}{L^2} - C e^2 \frac{8}{L}. \quad (46)$$

If we introduce atomic units ( $\hbar = e = m = 1$ ) so that length is measured in units of the Bohr radius we can plot the two energy curves,

$$E_{8d} = \frac{21}{L^2} - C \frac{4}{L}, \quad (47)$$

$$E_{8l} = \frac{48}{L^2} - C \frac{8}{L}, \quad (48)$$

and get the results of Fig. 2.

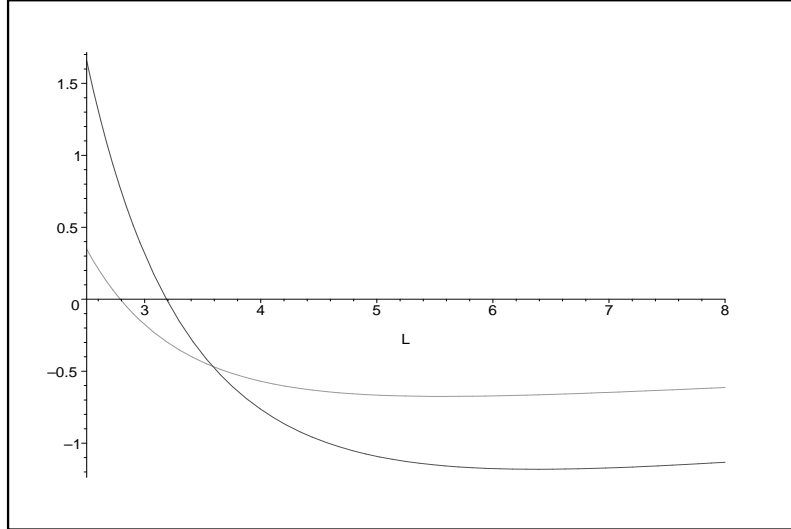


Figure 2: The energies of eight electrons in a cube of side  $L$  as function of  $L$  for the localized and delocalized cases, respectively. For  $L > 3.59$  the localized state has lower energy.

Finally we give the corresponding results for 16 electrons sharing orbitals pairwise. In the electrostatic energy one can then essentially change the particle charge  $e$  to  $2e$  and add the contributions from the repulsion within the pairs. This gives the two curves,

$$E_{16d} = \frac{117}{2L^2} - C \frac{8}{L}, \quad (49)$$

$$E_{16l} = \frac{192}{2L^2} - C \frac{16}{L}. \quad (50)$$

for the delocalized and localized energies respectively. These curves are plotted in Fig. 3.

One notes that the localized states always have lower electrostatic energy simply because in these states the electrons are better at avoiding each other. For small  $L$ -values the delocalized states always have lower energy because of the uncertainty principle. The curves in these plots resemble those of Wigner [11, 12] who predicted that localization gives lower energy in metals at low densities. This phenomenon is called Wigner crystallization.

## 7 Conclusions

I am not aware of any comparable study of the electrostatic interaction energies of homogeneous cubic charge distributions. The algebraic and com-

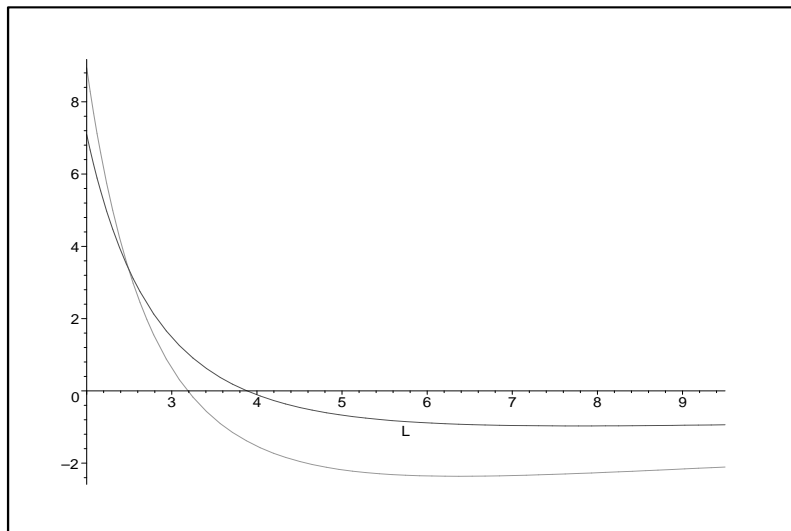


Figure 3: The energies of eight electron pairs in a cube of side  $L$  as function of  $L$  for the localized and delocalized cases, respectively. For  $L > 2.49$  the localized state has lower energy.

binatoric tricks used to eliminate the Coulomb singularities in the integrals seem partly new, as well as the result of Eq. (7). It is possible that these ideas can be generalized to more general integration problems involving the Coulomb singularity. It is a further bonus that these insights into the electrostatics of cubes and their sub-cubes can be used to make simple estimates for the Hartree energy of electrons distributed in cubes in different ways. Such simple model systems are of value for the qualitative understanding of more complex systems.

## References

- [1] H. Essén and A. B. Nordmark. Some results on the electrostatic energy of ionic crystals. *Canad. J. Chem.*, 74:885–891, 1996.
- [2] E. Moggia and B. Bianco. Closed form expression for the potential within a face centred cubic ionic crystal. *J. Electrostat. (Netherlands)*, 61:269–280, 2004.
- [3] J. Waldvogel. The Newtonian potential of a homogeneous cube. *Zeitschr. Angew. Math. Phys. (ZAMP)*, 27:867–871, 1976.
- [4] Y. T. Chen and A. Cook. *Gravitational Experiments in the Laboratory*. Cambridge University Press, Cambridge, 1993.

- [5] G. Hummer. Electrostatic potential of a homogeneously charged square and cube in two and three dimensions. *J. Electrostat. (Netherlands)*, 36:285–291, 1996.
- [6] Z. F. Seidov and P. I. Skvirsky. Gravitational potential and energy of homogeneous rectangular parallelepiped. e-print: astro-ph/0002496, at: Cornell University Library, arXiv.org e-print archive, Feb 2000.
- [7] D. K. Reitan and T. J. Higgins. Calculation of the electrical capacitance of a cube. *J. Appl. Phys.*, 22:223–226, 1951.
- [8] C.-O. Hwang and M. Mascagni. Electrical capacitance of the unit cube. *J. Appl. Phys.*, 95:3798–3802, 2004.
- [9] H. Raimes. *The Wave Mechanics of Electrons in Metals*. North Holland, Amsterdam, 1970.
- [10] H. Essén. A study of lattice and magnetic interactions of conduction electrons. *Phys. Scr.*, 52:388–394, 1995.
- [11] E. Wigner. On the interaction of electrons in metals. *Phys. Rev.*, 46:1002–1011, 1934.
- [12] E. Wigner. Effects of the electron interaction on the energy levels of electrons in metals. *Trans. Faraday Soc. (UK)*, 34:678–685, 1938.